AD 740616

AFOSR - TR - 72 - 0868

FINAL SCIENTIFIC REPORT OF GRANT AFOSR-68-1344

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March 27, 1972

Grant AFOSR-68-1344

THE ROLE OF THE ELECTRON IN BATTERIES
AND FUEL CELLS

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## DOCUMENT CONTROL DATA - R & D

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

| 1. ORIGINATING ACTIVITY (Corporate author) | 2a. REPORT SECURITY CLASSIFICATION |
|---|---|
| Department of Chemistry, Georgetown University, Washington D.C. 20007 | UNCLASSIFIED |
| | 2b. GROUP |

3. REPORT TITLE

THE ROLE OF THE ELECTRON IN BATTERIES AND FUEL CELLS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Scientific          Final

5. AUTHOR(S) *(First name, middle initial, last name)*

Robert de Levie

| 6. REPORT DATE | 7a. TOTAL NO. OF PAGES | 7b. NO. OF REFS |
|---|---|---|
| March     1972 | 8 | 19 |

| 8a. CONTRACT OR GRANT NO. | 9a. ORIGINATOR'S REPORT NUMBER(S) |
|---|---|
| AFOSR 68-1344 | |
| b. PROJECT NO. | |
| 9536 | |
| c. 61102F | 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* |
| d. 681303 | AFOSR - TR - 72 - 0 868 |

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY |
|---|---|
| TECH, OTHER | AF Office of Scientific Research (NC) 1400 Wilson Boulevard Arlington, Virginia 22209 |

13. ABSTRACT

This final scientific report briefly summarizes our results obtained in four different areas of electrochemical research: photo-emission of electrons from electrodes immersed in aqueous solution; electrocatalysis by anions adsorbed on electrodes; electrochemical theory; and membrane bio-electrochemistry. In all four areas, significant and novel contributions have been made.

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      Arlington, Virginia   22209

Re:   AFOSR Grant 68-1344
      Robert de Levie, principal investigator

FINAL SCIENTIFIC REPORT

This report covers the period from August 1, 1967 through December 31, 1971. Our research during this period can conveniently be classified in separate categories, and this report is organized accordingly.

Photo-emission

Ultraviolet light focussed on a mercury electrode in a non-absorbing solution gives rise to a current in an external polarographic circuit. Such currents were first described by Berg and by Barker in the early sixties, and further studied by M. Heyrovský and by Delahay. Each of these four workers proposed a different explanation for the observed photo-effect. We set out to develop instrumentation to examine this electrochemical photo-effect in more detail than had been possible so far with the specific aim of accurately determining the threshold potential.

Using a combination of phase-sensitive detection and careful iR compensation through positive feedback, we first developed instrumentation[1,3] with the necessary sensitivity and precision. With this equipmen photocurrents of the order of $10^{-9}$A can be measured in the presence of noncoherent charging currents of well over $10^{-7}$A.

A preliminary study of the photocurrents, using $N_2O$ as electron scavenger, in conjunction with various organic adsorbents, indicated that charge-transfer interaction as proposed by Heyrovský was a most unlikely explanation for the observed effects[3]. Also, a study of the potential-dependence of the photocurrents showed[3] that the theory just then developed by Levich et al. represents the data more accurately than the earlier model of Delahay, but that neither one could account for the dependence of the threshold potential on light energy.

Careful further studies[15] showed that the observed photocurrents could be represented accurately by an extension of the so-called "five-halves law," and that such extension also overcame the difficulties with the dependence of the threshold potential on light frequency.

Our experiments with ultraviolet and visible light were extended to include excitation with an argon-ion laser beam, and we developed numerical procedures for the accurate determination of threshold potentials[15]. Unfortunately, the precision attainable with the above refinements in instrumentation and data analysis is still insufficient to determine threshold potentials to the level required for their use as reference potentials of thermodynamic significance.

## Electrocatalysis

The novel instrumentation described above turned out to be equally valuable for more "traditional" electrochemical studies, and we applied it to an investigation of the polarographic reduction of indium ions from aqueous solutions of thiocyanate. This system exhibits a curious "minimum" in its diffusion-limited current, for which various qualitative explanations had been advanced. We measured both the dc and ac polarographic currents, and were able to show the quantitative correlation between the polarographic minimum and the measured negative admittance[4]. Subsequently, we introduced the thermodynamic concept of surface activity which allowed us to explain the observed behavior in terms of a simple mechanism analogous to ligand bridging[6]. This is the first time that such a mechanism has been demonstrated for substitution-labile ions, and it now appears to be a fairly common pathway for electrode reactions[13], which is even involved in the oft-studied hydrogen evolution reaction[8].

## Electrochemical theory

The above developments led to the concept of coupling between interfacial and transport impedances[5,11] which has recently been extended[14] to include the coupling between faradaic and double layer charging currents

discovered by Delahay. We also contributed what appears to be the first thermodynamic treatment of the case intermediate between the ideal polarized and the reversible electrode[2], and we have pointed out some general aspects of ionic adsorption which we believe to have far-reaching consequences for thermodynamic investigations of adsorption isotherms[13]. Finally, our work on the theory of the faradaic admittance[4,5] led to a simple method to calculate reversible half-wave potentials from quasi-reversible polarographic waves[10].

## Bioelectrochemistry

Our experimental and theoretical work on negative admittances[4,5,11,12] led to an interest in electrochemical oscillators. These are not only common to the surfaces of passivating or corroding metals, but also to many biological membranes. We studied and explained electrochemical oscillations on mercury[7], and have recently started to investigate the basic processes involved in ionic movement through ultrathin "bi-layer" membranes.[17-19] Here, we have studied and clarified the equilibrium behavior of thin semi-permeable membranes as occur in biological systems.[18] Subsequently, we have been able to express the non-equilibrium steady-state behavior in terms of equilibrium properties like potential and intrinsic conductance, and ionic current density.[19] This description goes a long way towards explaining experimentally observed current-voltage relationships on bio-membranes, and is at present being extended to include mass transport and double layer effects outside the membrane proper.

## Miscellaneous

Finally, several peripherally related papers on graphical representations of complicated equilibria[9] and on the specific adsorption of trifluoromethanesulfonate ions on mercury[16] were prepared during the report period.

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COMPLETED PROJECT SUMMARY

AFOSR Grant 68-1344

## Photo-emission

* Instrumentation has been developed which can measure small photo-currents in the presence of much larger charging and faradaic currents. Overall noise (from instrument plus electrochemical cell) is below 1 nA top-to-top. The instrument can also record the in-phase and quadrature components of the faradaic admittance, as well as the dc polarogram. Positive feedback is used to minimize iR drop, and methods are given to measure and correct for any remaining iR drop.

* Photocurrents on a dropping mercury electrode in non-absorbing aqueous solutions can not only be obtained by ultraviolet excitation but also by irradiation with visible light. Photocurrent-potential curves are often structureless and monotonically increasing, and are fairly well described as proportional to $(E-E_T)^{5/2}$ where $E_T$ is the threshold potential.

* The dependence of threshold potential on light energy as measured between 313 and 579 nm (4.0 to 2.1 eV) is anomalous when $N_2O$ is used as a scavenger. With no other known scavenger can a comparably large range of potentials be scanned to determine whether this result is particular to the use of $N_2O$ with its limited solubility, or reflects a basic flaw in the model.

* The effects of specifically adsorbed alcohols have been studied. The photocurrents are influenced but little by the presence of monolayer films of electron solvents. Especially interesting is the observation of streaming in the adsorption-desorption region of decanol, since polarographic maxima are often thought to be related to the flow of faradaic current.

* Even with extensive use of computer-analysis of a large volume of precise data, estimates of the threshold potential $E_T$ have an accuracy of at best $\pm 10$ mV. Thus, $E_T$ cannot at present be used as a practical reference potential of thermodynamic significance.

## Electrocatalysis

*   As long as the pH is sufficiently low to prevent its hydrolysis, indium(III) is not reduced from aqueous solutions in the absence of electrocatalysts. In the presence of one such catalyst, thiocyanate, the reduction rate is enhanced to such an extent that a reversible polarographic wave is obtained with catalyst concentrations of 10 mM or higher. The mechanism of this catalysis has been shown to include two thiocyanate ions adsorbed on the electrode surface, and to involve indium ions with no or small thiocyanate coordination in the aqueous solution.

*   The above electrocatalytic pathway involving ligand bridging of adsorbed anions is likewise involved in the reduction of indium from halide-containing solutions. Nickel, zinc and hydrogen ions exhibit similar reduction pathways.

*   The catalytic effect of adsorbed ions is not proportional to their surface excess, but rather to a quantity called "surface activity," which is a novel thermodynamic quantity related to the ionic adsorption isotherm.

*   The adsorption of ions has been shown to depend markedly on the outer Helmholtz potential. This explains the effect of weakly adsorbed electrolytes like NaF on ionic adsorption isotherms.

## Electrochemical theory

*   It has been shown that the charge transfer resistance depends on the derivatives of rate constants with respect to potential. From this, the relations between the dc and ac polarographic responses have been obtained and experimentally verified. These calculations also provide the explanation for the occurrence of negative faradaic admittances of several types.

*   The interfacial and transport impedances have been shown to be coupled intimately, to the extent that, e.g., a negative charge transfer resistance makes the Warburg impedance negative. This coupling is a

quite general phenomenon.

* The theoretical expressions derived for ac polarography have led to the development of a more accurate method of determining reversible halfwave potentials from quasi-reversible polarographic waves.

## Bioelectrochemistry

* The conditions necessary for the generation of electrochemical oscillations have been obtained. Steady-state current-voltage curves have been shown to be insufficient in themselves to draw conclusions about oscillatory behavior. Application of the Llewellyn criterion does provide the necessary information.

* Electrochemical oscillations of variable frequency have been generated at the mercury/aqueous solution interface by using the above-mentioned principles as guidelines. It has been shown that the addition of resistance in series with the electrochemical cell can make an otherwise stable system oscillatory. This observation, which is of interest in the comparison of potentiostatic and galvanostatic experiments, is directly interpretable in terms of the Llewellyn criterion mentioned above.

The equilibrium distribution of membrane-permeable ions inside an ultrathin bilayer membrane has been calculated. At high ionic concentrations, two essentially separate double layers are found inside the membrane, whereas only one space-charge region is obtained at low ionic concentrations.

* Considerations of dielectric breakdown have led to an estimate of the maximum ionic concentration of about 10 mM possible in bilayer membranes.

* The mathematical description of steady-state ionic transport through bilayer membranes has been given, using numerical solution of a derived closed-form algebraic expression. The results show that the current-voltage behavior can be described to sufficient precision in terms of an intrinsic equilibrium conductance.

* The intrinsic equilibrium conductance is a linear function of concentration at low ionic content of the membrane, whereas it reaches a limiting value at high ionic membrane concentrations.

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